TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		Attorney's Docket Number 05725.0489 U.S. Application No. 09/424116
...ional Application. No.	International Filing Date	Priority Date Claimed
FR99/00542	March 11, 1999	March 20, 1998

...e of Invention:
...IDATION DYEING COMPOSITION FOR KERATINOUS FIBRES CONTAINING A 3-AMINOPYRIDINE AZO ...ERIVATIVE AND DYEING METHOD USING SAID COMPOSITION

Applicant(s) For DO/EO/US:
G...d LANG, Jean COTTERET and Mireille MAUBRU

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. [ ] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [ ] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [ ] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [X] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [X] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [X] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.

16. [ ] Other items or information:
    a. [ ] Verified Small Entity Statement.
    b. [ ] Copy of Notification of Missing Requirements.
    c. [X] New Abstract.

420 Rec'd PCT/PTO 19 NOV 1999

APPLICATION NO.	INTERNATIONAL APPLICATION NO.	ATTORNEY DOCKET NUMBER
09/424116	PCT/FR99/00542	05725.0489

The following fees are submitted:	CALCULATIONS
Basic National Fee (37 CFR 1.492(a)(1)-(5)):	
Search Report has been prepared by the EPO or JPO.....$840.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482).....$670.00	
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....$760.00	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....$970.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4).....$ 96.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 840.00
Surcharge of $130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$

Claims	Number Filed	Number Extra	Rate	
Total Claims	35 -20=	15	X $18.00	$ 270.00
Independent Claims	3 - 3=		X $78.00	$
Multiple dependent claim(s) (if applicable)			+$260.00	$
TOTAL OF ABOVE CALCULATIONS =				**$1,110.00**
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28)				$
SUBTOTAL =				**$1,110.00**
Processing fee of $130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			+	$
TOTAL NATIONAL FEE =				**$1,110.00**
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31).			$40.00 per property +	$
TOTAL FEES ENCLOSED =				**$1,110.00**
Amount to be refunded				$
charged				$

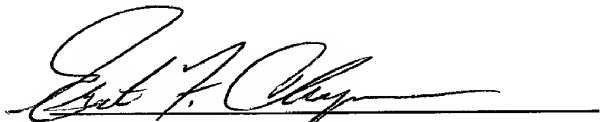
a. [X] A check in the amount of **$1,110.00** to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 06-0916. A duplicate copy of this sheet is enclosed.

The Commissioner is hereby authorized to charge any other fees due under 37 C.F.R. §1.16 or §1.17 during the pendency of this application to our Deposit Account No. 06-0916.

SEND ALL CORRESPONDENCE TO:
Finnegan, Henderson, Farabow Garrett & Dunner, L.L.P.
1300 I Street, N.W.
Washington, D.C. 20005-3315
EFC/FPD/rgm



Ernest F. Chapman
Reg. No. 25,961

Submitted: November 19, 1999

PATENT

Attorney Docket No. 05725.0489-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re National Stage of International Application No. PCT/FR99/00542 of:

Gérard LANG et al.

Serial No.: Unassigned — Group Art Unit: Unassigned

PCT Filed: March 11, 1999 — Examiner: Unassigned

National Stage Entry: November 19, 1999

For: OXIDATION DYEING COMPOSITION FOR KERATINOUS FIBRES CONTAINING A 3-AMINOPYRIDINE AZO DERIVATIVE AND DYEING METHOD USING SAID COMPOSITION

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the above application, please amend this application as follows:

IN THE CLAIMS:

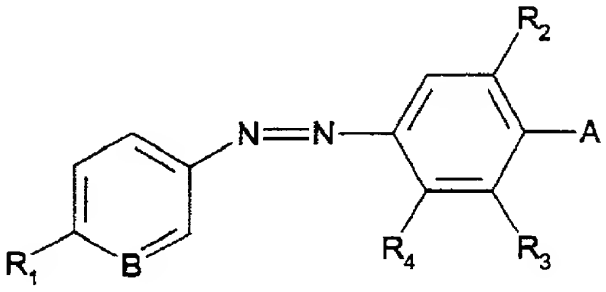
Please cancel claims 1 to 25 without prejudice or disclaimer and replace them with new claims 26 to 60 as follows:

LAW OFFICES
FINNEGAN, HENDERSON, FARABOW, GARRETT, & DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

-- 26. A composition for the oxidation dyeing of keratin fibers comprising:

a) at least one oxidation base, and

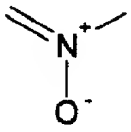
b) as direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I):



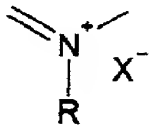
(I)

in which:

- B is chosen from formula (Ia) and (Ib):



(Ia)



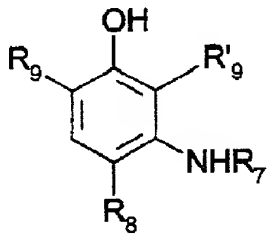
(Ib)

- R is a C_1-C_4 alkyl radical;

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- R_1 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, and a C_1-C_4 alkoxy radical;
- R_2 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, and a C_1-C_4 alkoxy radical;
- R_4 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a nitro, an amino radical and a (C_1-C_4)acylamino radical;
- R_3 is a hydrogen atom, or R_4 and R_3 together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;
- A is a residue $-NR_5R_6$ in which R_5 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical and C_2-C_4 polyhydroxyalkyl radical and R_6 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a phenyl ring and a $-CH_2-SO_3Na$ radical;
- X^- is chosen from a monovalent anion and a divalent anion, and

c) at least one coupler chosen from a meta-aminophenol derivative of formula (II), and an addition salt thereof with an acid:



(II)

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

in which:

- R_7 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical and a C_1-C_4 monoaminoalkyl radical;
- R_8 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, and a C_1-C_4 alkoxy radical;
- R_9 and R'_9, which are identical or different, are chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 alkoxy radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a C_1-C_4 monohydroxyalkoxy radical and a C_2-C_4 polyhydroxyalkoxy radical;

with the proviso that at least one of the substituents R_7, R_8, R_9 and R'_9 is not a hydrogen atom.

27. A composition according to Claim 26, wherein said keratin fibres are human keratin fibres.

28. A composition according to Claim 27, wherein said human keratin fibres are human hair.

29. A composition according to Claim 26, wherein said halogen atom is chosen from chlorine, bromine and fluorine.

30. A composition according to Claim 26, wherein said X^- is chosen from a halogen atom, a hydroxide, a hydrogen sulfate and a (C_1-C_6)alkyl sulfate.

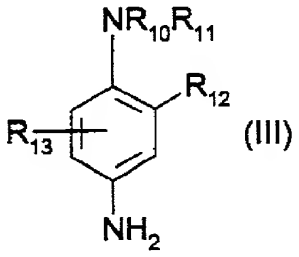
LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

31. A composition according to Claim 30, wherein said halogen atom is chosen from chlorine, bromine, fluorine and iodine.

32. A composition according to Claim 30, wherein said (C_1-C_6)alkyl sulfate is chosen from a methyl sulfate and an ethyl sulfate.

33. A composition according to Claim 26, wherein said at least one oxidation base is chosen from a para-phenylenediamine, a double base, a para-aminophenol, an ortho-aminophenol and heterocyclic oxidation bases.

34. A composition according to Claim 33, wherein said para-phenylenediamine is chosen from a compound of formula (III), and an addition salt thereof with an acid:



(III)

in which:

- R_{10} is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_4)alkoxy(C_1-C_4)alkyl radical, a C_1-C_4 alkyl radical substituted with a nitrogenous group, phenyl and 4'-aminophenyl;

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- R_{11} is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_4)alkoxy(C_1-C_4)alkyl radical and a C_1-C_4 alkyl radical substituted with a nitrogenous group;
- R_{12} is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_1-C_4 hydroxyalkoxy radical, an acetylamino(C_1-C_4)alkoxy radical, a mesylamino(C_1-C_4)alkoxy radical and a carbamoylamino(C_1-C_4)alkoxy radical,
- R_{13} is chosen from a hydrogen atom, a halogen atom and a C_1-C_4 alkyl radical.

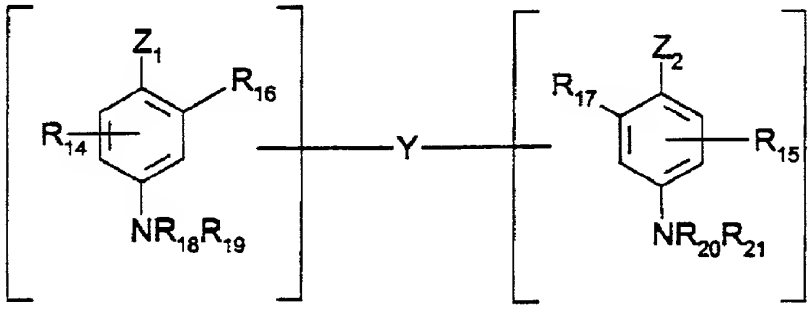
35. A composition according to Claim 34, wherein said halogen atom is chosen from chlorine, bromine, iodine and fluorine.

36. A composition according to Claim 33, wherein said para-phenylenediamine of formula (III) is chosen from para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(b-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(b-hydroxyethyl)amino-2-chloroaniline, 2-b-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(b-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-(b-

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

hydroxyethyl)-para-phenylenediamine, N-(b,g-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-b-hydroxyethyloxy-para-phenylenediamine, 2-b-acetylaminoethyloxy-para-phenylenediamine, N-(b-methoxyethyl)-para-phenylenediamine, and addition salts thereof with an acid.

37. A composition according to Claim 33, wherein said double base is chosen from a compound of formula (IV), and an addition salt thereof with an acid:



(IV)

in which:

- Z_1 and Z_2, which are identical or different, are chosen from a hydroxyl radical and an $-NH_2$ radical, each of which is unsubstituted or substituted with a C_1-C_4 alkyl radical or with a linker arm Y;

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- R_{14} and R_{15} are chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a C_1-C_4 aminoalkyl radical and a linker arm Y;
- R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21}, which are identical or different, are chosen from a hydrogen atom, a linker arm Y and a C_1-C_4 alkyl radical;
- said linker arm Y is chosen from a linear alkylene chain and a branched alkylene chain, each chain comprising from 1 to 14 carbon atoms, which can be interrupted or terminated with at least one nitrogenous group, at least one hetero atom, or a mixture thereof and optionally substituted with at least one hydroxyl radical or a C_1-C_6 alkoxy radical;

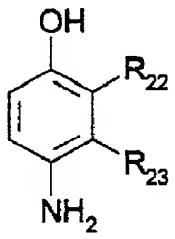
with the proviso that said compounds of formula (IV) comprise only one linker arm Y per molecule.

38. A composition according to Claim 37, wherein said at least one hetero atom is chosen from oxygen, sulphur and nitrogen.

39. A composition according to Claim 37, wherein said double base of formula (IV) is chosen from N,N'-bis(b-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(b-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(b-hydroxyethyl)-N,N'-bis(4-aminophenyl) tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine, 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and an addition salt thereof with an acid.

LAW OFFICES
FINNEGAN, HENDERSON, FARABOW, GARRETT, & DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

40. A composition according to Claim 33, wherein said para-aminophenol is chosen from a compound of formula (V), and an addition salt thereof with an acid:



(V)

in which:

- R_{22} is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a (C_1-C_4)alkoxy(C_1-C_4)alkyl radical, a C_1-C_4 aminoalkyl radical and a hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radical,
- R_{23} is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a C_1-C_4 aminoalkyl radical, a cyano(C_1-C_4)alkyl radical and a (C_1-C_4)alkoxy(C_1-C_4)alkyl radical,

with the proviso that at least one of the substituents R_{22} and R_{23} is a hydrogen atom.

41. A composition according to Claim 40, wherein said para-aminophenol of formula (V) is chosen from para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

amino-2-(b-hydroxyethylaminomethyl)phenol, 4-amino-2-fluorophenol, and an addition salt thereof with an acid.

42. A composition according to Claim 33, wherein said ortho-aminophenol is chosen from 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-aminophenol, and an addition salt thereof with an acid.

43. A composition according to Claim 33, wherein said heterocyclic oxidation bases are chosen from a pyridine derivative, a pyrimidine derivative, a pyrazole derivative, and an addition salt thereof with an acid.

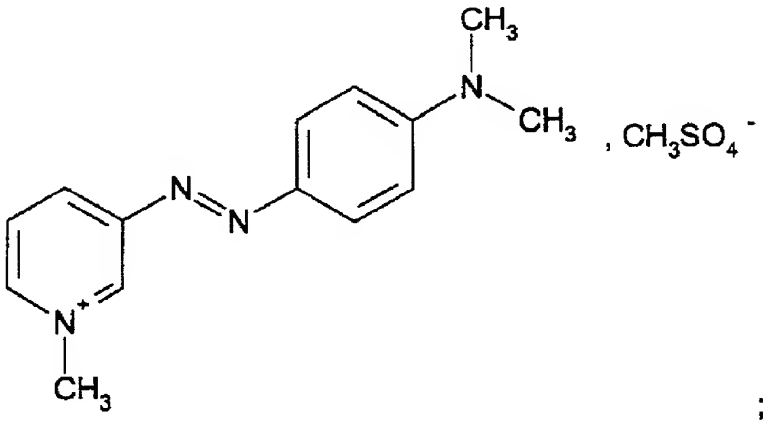
44. A composition according to Claim 26, wherein said at least one oxidation base is present in an amount ranging from about 0.0005 to about 12% by weight relative to the total weight of the dye composition.

45. A composition according to Claim 44, wherein said at least one oxidation base is present in an amount ranging from about 0.005 to about 6% by weight relative to the total weight of the dye composition.

46. A composition according to Claim 26, wherein said at least one 3-aminopyridine derivative of formula (I) is chosen from:

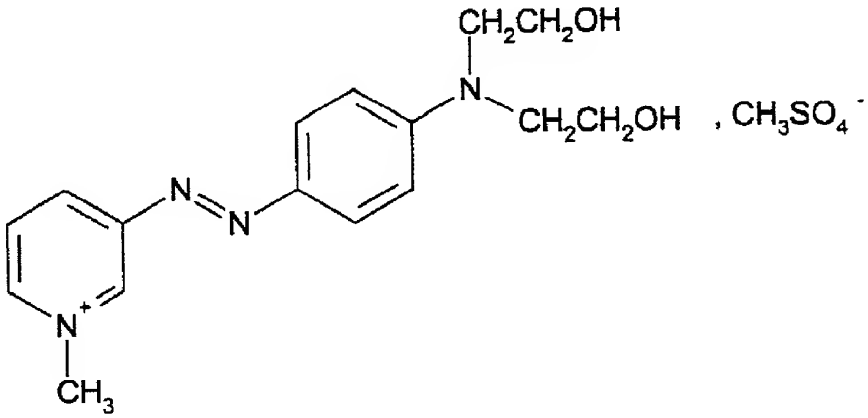
- 4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000



;

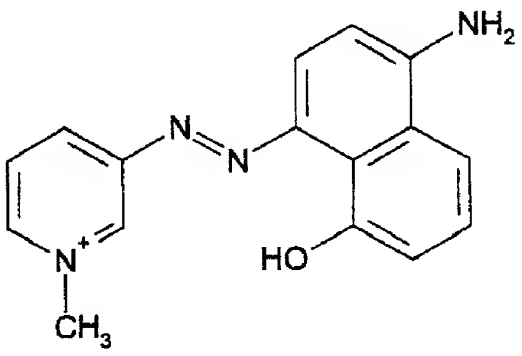
- 4'-bis(b-hydroxyethyl)aminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



;

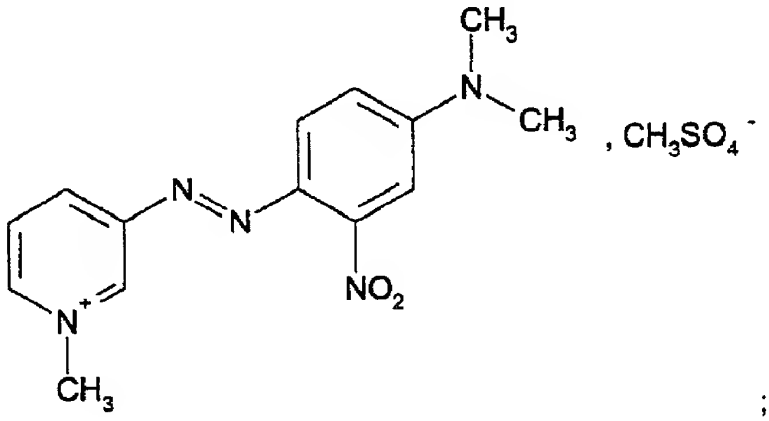
LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- 4'-amino-8'-hydroxynaphthalene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



;

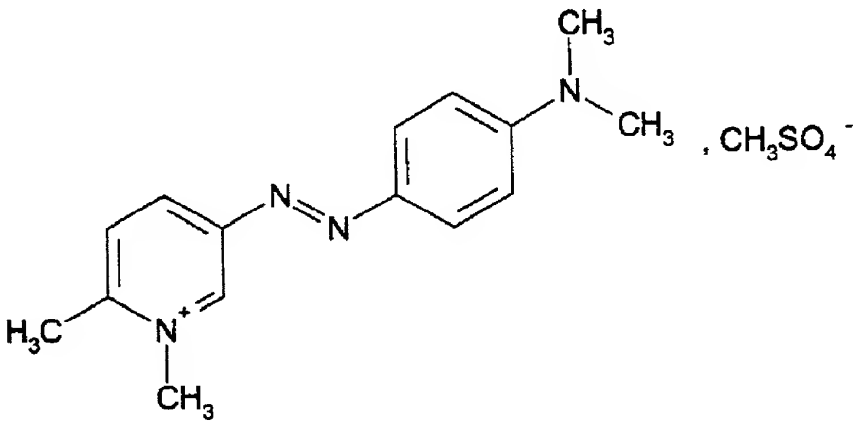
- 4'-dimethylamino-2'-nitrobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



;

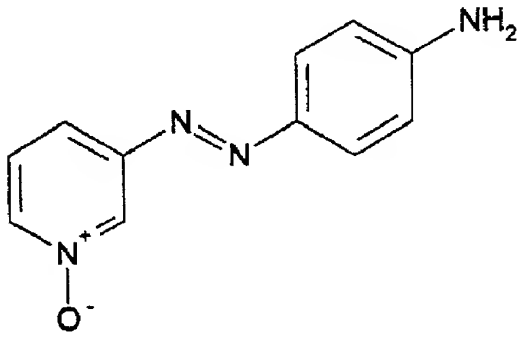
LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- 4'-dimethylaminobenzene-1'-azo-1,6-dimethyl-3-pyridinium methosulphate of formula:



;

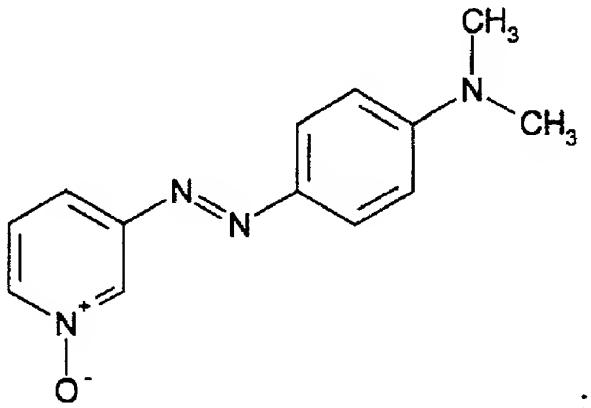
- 4'-aminobenzene-1'-azo-3-pyridine N-oxide of formula:



;

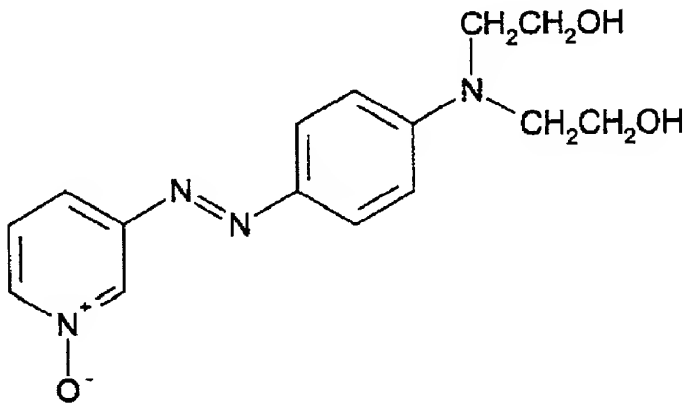
LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- 4'-dimethylaminobenzene-1'-azo-3-pyridine N-oxide of formula:



;

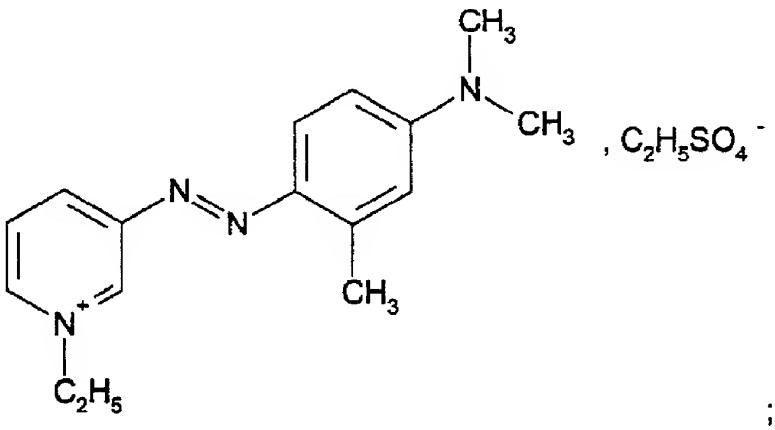
- 4'-N,N-bis(b-hydroxyethyl)aminobenzene-1'-azo-3-pyridine N-oxide of formula:



;

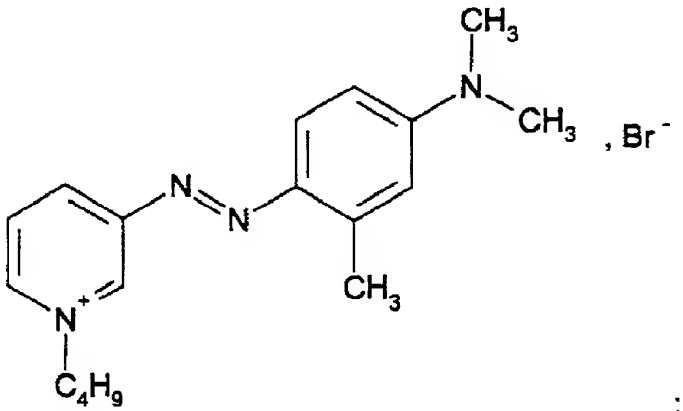
LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:



;

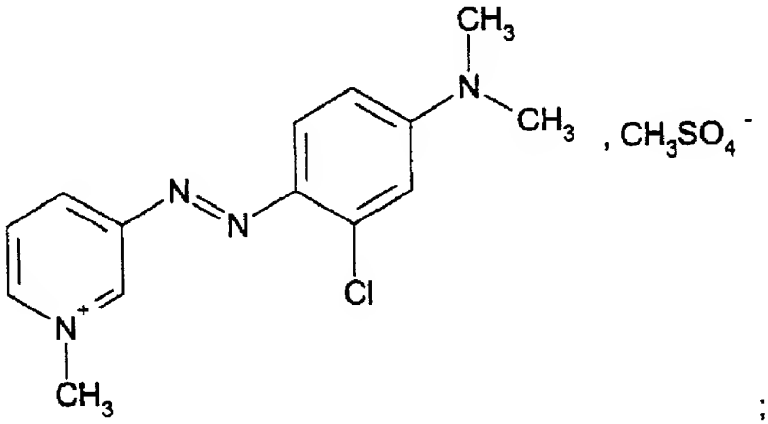
- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-butyl-3-pyridinium bromide of formula:



;

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

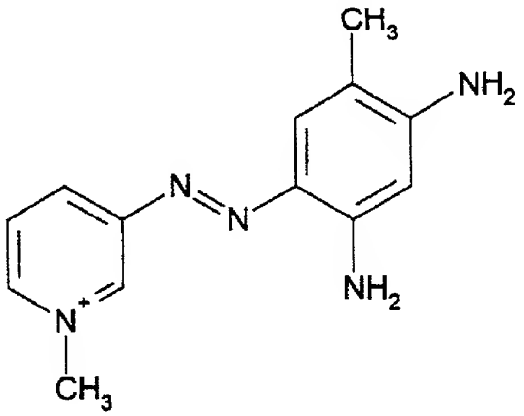
- 4'-dimethylamino-2'-chlorobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



;

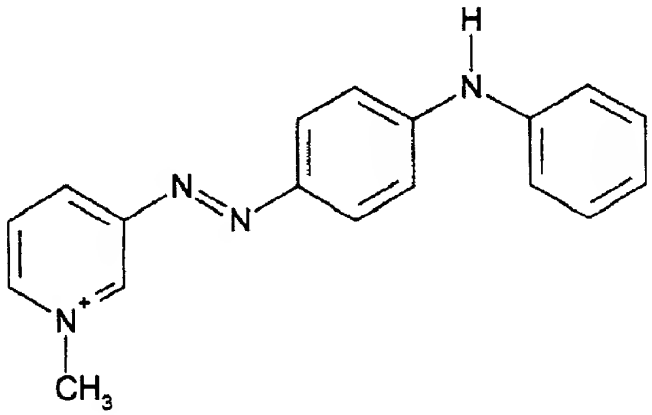
- 2',4'-diamino-5'-methylbenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000



;

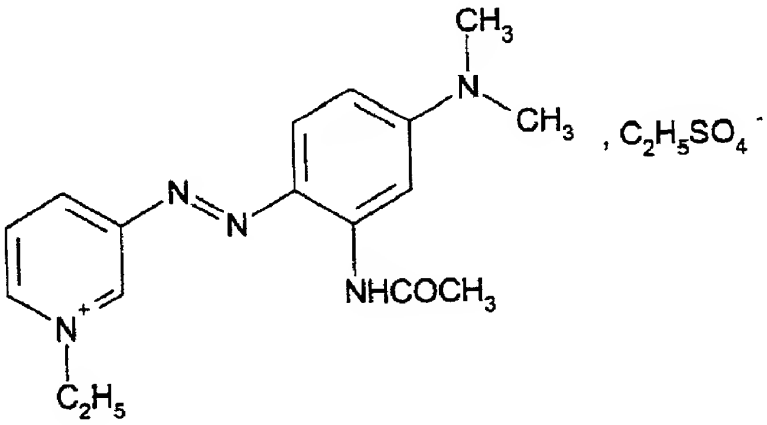
- 4'-phenylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



;

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

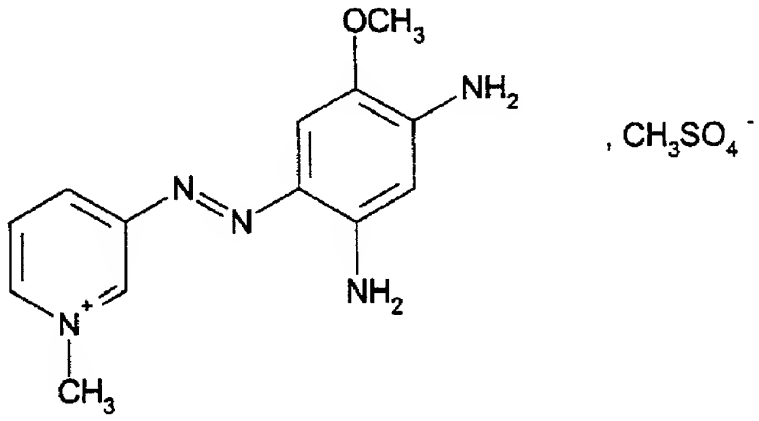
- 2'-acetylamino-4'-dimethylaminobenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:



;

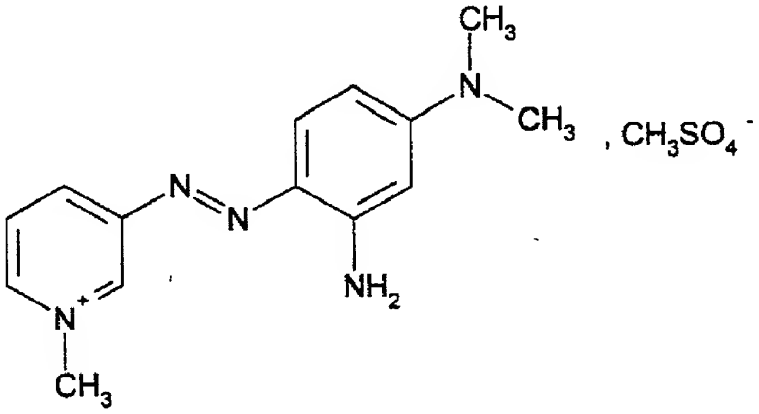
- 2',4'-diamino-5'-methoxybenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000



and

- 2'-amino-4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

47. A composition according to Claim 26, wherein said at least one 3-amino-pyridine derivative of formula (I) is present in an amount ranging from about 0.001 to about 10% by weight relative to the total weight of the dye composition.

48. A composition according to Claim 47, wherein said at least one 3-aminopyridine derivative of formula (I) is present in an amount ranging from about 0.01 to about 5% by weight relative to the total weight of the dye composition.

49. A composition according to Claim 26, wherein said meta-aminophenol derivative of formula (II) is chosen from 5-amino-2-methoxyphenol, 5-amino-2-(b-hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-(b-hydroxyethyl)amino-2-methylphenol, 5-N-(b-hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol, 5-(g-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-amino-6-chlorophenol, 3-(b-aminoethyl)amino-6-chlorophenol, and an addition salt thereof with an acid.

50. A composition according to Claim 26, wherein said meta-aminophenol derivative of formula (II) is present in an amount ranging from about 0.0001 to about 10% by weight relative to the total weight of the dye composition.

51. A composition according to Claim 50, wherein said meta-aminophenol derivative of formula (II) is present in an amount ranging from about 0.005 to about 5% by weight relative to the total weight of the dye composition.

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

52. A composition according to Claim 26, further comprising at least one coupler other than said meta-aminophenol derivative of formula (II), at least one direct dye other than said 3-aminopyridine derivatives of formula (I), or a mixture thereof.

53. A composition according to Claim 26, wherein said addition salt with an acid is chosen from a hydrochloride, a hydrobromide, a sulphate, a tartrate, a lactate and an acetate.

54. A composition according to Claim 26, wherein said composition is in a medium suitable for dyeing.

55. A composition according to Claim 54, wherein said medium suitable for dyeing comprises water or a mixture of water and at least one organic solvent.

56. A composition according to Claim 26, wherein said composition has a pH ranging from about 3 to about 12.

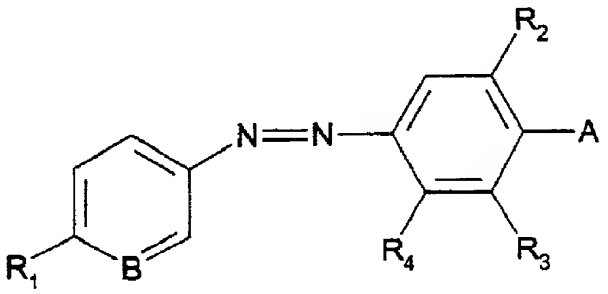
57. A process for dyeing keratin fibers comprising:

1) applying at least one dye composition to keratin fibers, wherein said at least one dye composition comprises

a) at least one oxidation base,

b) as a direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I):

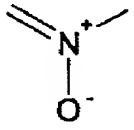
LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000



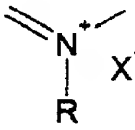
(I)

in which:

- B is chosen from formula (Ia) and (Ib):



(Ia)



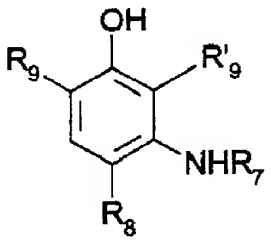
(Ib)

- R is a C_1-C_4 alkyl radical;
- R_1 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, and a C_1-C_4 alkoxy radical;
- R_2 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, and a C_1-C_4 alkoxy radical;

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- R_4 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a nitro, an amino radical and a (C_1-C_4)acylamino radical;
- R_3 is a hydrogen atom, or R_4 and R_3 together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;
- A is a residue $-NR_5R_6$ in which R_5 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical and a C_2-C_4 polyhydroxyalkyl radical and R_6 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a phenyl ring and a $-CH_2-SO_3Na$ radical;
- X^- is chosen from a monovalent anion and a divalent anion, and

c) at least one coupler chosen from a meta-aminophenol derivative of formula (II), and an addition salt thereof with an acid:



(II)

in which:

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- R_7 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical and a C_1-C_4 monoaminoalkyl radical;
- R_8 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical and a C_1-C_4 alkoxy radical;
- R_9 and R'_9, which are identical or different, are chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 alkoxy radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a C_1-C_4 monohydroxyalkoxy radical and a C_2-C_4 polyhydroxyalkoxy radical;

with the proviso that at least one of the substituents R_7, R_8, R_9 and R'_9 is not a hydrogen atom; and

2) developing a color at an acidic, neutral or alkaline pH with the aid of an oxidizing agent, wherein said oxidizing agent is added to said at least one dye composition at the time of application of said at least one dye composition, or wherein said oxidizing agent is present in an oxidizing composition, and wherein said oxidizing composition is applied simultaneously or sequentially with said at least one dye composition.

58. A process according to Claim 57, wherein said oxidizing agent present in the oxidizing composition is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts, peracids and enzymes.

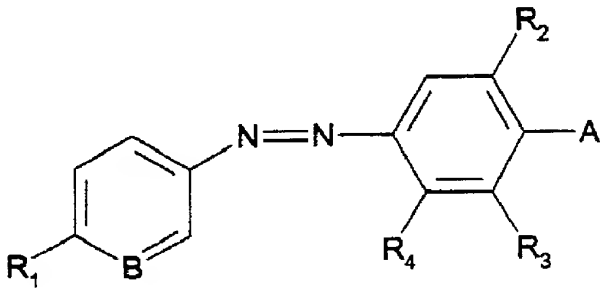
59. A process according to Claim 58, wherein said persalts are chosen from perborates, percarbonates and persulphates.

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

60. A multi-compartment dyeing device or kit comprising at least two compartments, wherein one compartment comprises an oxidizing composition, and another compartment comprises at least one dye composition, wherein said at least one dye composition comprises

a) at least one oxidation base,

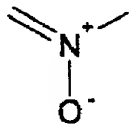
b) as direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I):



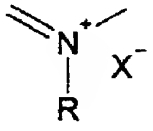
(I)

in which:

- B is chosen from formula (Ia) and (Ib):



(Ia)

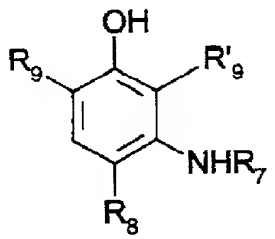


(Ib)

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

- R is a C_1-C_4 alkyl radical;
- R_1 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, and a C_1-C_4 alkoxy radical;
- R_2 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, and a C_1-C_4 alkoxy radical;
- R_4 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a nitro, an amino radical and a (C_1-C_4)acylamino radical;
- R_3 is a hydrogen atom, or R_4 and R_3 together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;
- A is a residue $-NR_5R_6$ in which R_5 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical and C_2-C_4 polyhydroxyalkyl radical and R_6 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a phenyl ring and a $-CH_2-SO_3Na$ radical;
- X^- is chosen from a monovalent anion and a divalent anion, and

c) at least one coupler chosen from a meta-aminophenol derivative of formula (II), and an addition salt thereof with an acid:



(II)

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

in which:

- R_7 is chosen from a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical and a C_1-C_4 monoaminoalkyl radical;
- R_8 is chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical and a C_1-C_4 alkoxy radical;
- R_9 and R'_9, which are identical or different, are chosen from a hydrogen atom, a halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 alkoxy radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a C_1-C_4 monohydroxyalkoxy radical and a C_2-C_4 polyhydroxyalkoxy radical;

with the proviso that at least one of the substituents R_7, R_8, R_9 and R'_9 is not a hydrogen atom. –

REMARKS

Claims 26-60 are pending. Claims 1–25 have been canceled without prejudice or disclaimer, and rewritten as new claims 26-60 to more particularly point out and distinctly claim that which Applicant considers to be the invention, and to place the claims in better conformance with U.S. patent practice. Support for new claims 26-60 can be found throughout the specification, and in original claims 1-25. Thus, no new matter has been added by these amendments. Accordingly, Applicants now await an action on the merits.

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

Please grant any extensions of time required to enter this Preliminary Amendment and charge any additional required fees to our deposit account Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.

By: _____
Mark D. Sweet
Reg. No. 41,469

Dated: November 19, 1999

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N. W.
WASHINGTON, DC 20005
202-408-4000

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES AND DYEING PROCESS USING THIS COMPOSITION

The invention relates to a composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one oxidation base, at least one 3-aminopyridine derivative as direct dye, and at least one substituted meta-aminophenol as coupler, as well as to the dyeing process using this composition.

It is known practice to dye keratin fibres, and in particular human hair, with dye compositions containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic bases, which are generally referred to as oxidation bases. Oxidation dye precursors, or oxidation bases, are colourless or weakly coloured compounds which, when combined with oxidizing products, can give rise to coloured compounds and dyes by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or colour modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used as regards the oxidation bases and couplers allows a wide range of colours to be obtained.

It is also known that, in order to vary the shades obtained even more and to give them glints, it is possible to use, in combination with the oxidation dye precursors and couplers, direct dyes, i.e. coloured substances which provide a coloration in the absence of an oxidizing agent.

The great majority of these direct dyes belong to the family of nitrobenzene compounds and have the drawback, when they are incorporated into dye compositions, of leading to colorations that are not sufficiently fast, in particular with respect to shampoos.

The so-called "permanent" coloration obtained by means of these oxidation dyes must moreover satisfy a certain number of requirements. Thus, it must be able to give shades of the desired intensity and it must be able to withstand external agents (light, bad weather, washing, permanent-waving, perspiration and rubbing).

The dyes must also make it possible to cover white hair, and, finally, they must be as unselective as possible, i.e. they must give the smallest possible differences in colour all the way along the same keratin fibre, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

Compositions for the oxidation dyeing of keratin fibres containing a combination of a benzenic oxidation base, a direct dye of the 3-aminopyridine family and an unsubstituted meta-aminophenol as coupler have already been proposed, in particular in patent application FR-A-2,285,851. However, the colorations obtained using such compositions are not entirely satisfactory, in particular from the point of view of their chromaticity and their fastness.

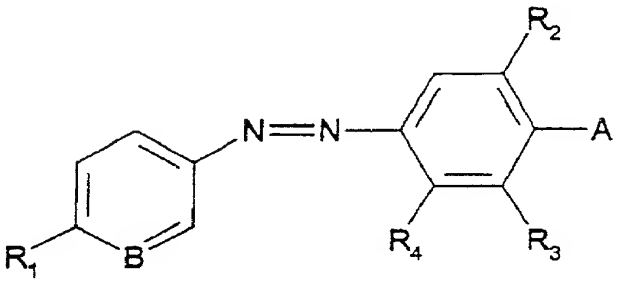
The Applicant has now discovered that it is possible to obtain novel dyes which are capable of giving intense and chromatic colorations, which show little selectivity and which satisfactorily withstand the various attacking factors to which the fibres may be subjected, by combining at least one oxidation base, at least one suitably selected 3-aminopyridine derivative as direct dye, and at least one suitably selected meta-aminophenol derivative.

This discovery forms the basis of the present invention.

A first subject of the invention is thus a composition for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing:

- at least one oxidation base,

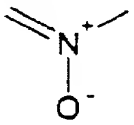
- as direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I) below:



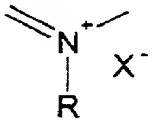
(I)

in which:

- B represents a group of formula (Ia) or (Ib) below:



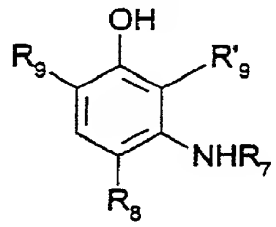
(Ia)



(Ib)

- R represents a C_1-C_4 alkyl radical;
- R_1 represents a hydrogen or halogen atom such as chlorine, bromine or fluorine, or a C_1-C_4 alkyl or C_1-C_4 alkoxy radical;
- R_2 represents a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 alkoxy radical;
- R_4 represents a hydrogen or halogen atom such as chlorine, bromine or fluorine, or a C_1-C_4 alkyl, nitro, amino or (C_1-C_4)acylamino radical;
- R_3 represents a hydrogen atom or else R_4 and R_3 together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;

- A represents a residue $-NR_5R_6$ in which R_5 represents a hydrogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical; R_6 represents a hydrogen atom, a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical, a phenyl ring or a $-CH_2-SO_3Na$ radical;
- X^- represents a monovalent or divalent anion and is preferably chosen from a halogen atom such as chlorine, bromine, fluorine or iodine, a hydroxide, a hydrogen sulphate or a $(C_1$-$C_6)$alkyl sulphate such as, for example, a methyl sulphate or an ethyl sulphate, and
- at least one coupler chosen from the meta-aminophenol derivatives of formula (II) below, and the addition salts thereof with an acid:



(II)

in which:

- R_7 represents a hydrogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl or C_1-C_4 monoaminoalkyl radical;
- R_8 represents a hydrogen atom, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or a halogen atom chosen from chlorine, bromine and fluorine,

- R_9 and R'_9, which may be identical or different, represent a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 monohydroxyalkoxy or C_2-C_4 polyhydroxyalkoxy radical;

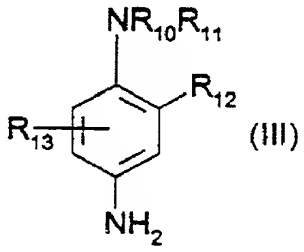
it being understood that at least one of the radicals R_7, R_8, R_9 and R'_9 is other than a hydrogen atom.

The dye composition in accordance with the invention gives intense, chromatic colorations which show little selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather, and with respect to perspiration and the various treatments to which the hair may be subjected. These properties are particularly noteworthy as regards the chromaticity.

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this dye composition.

The nature of the oxidation base(s) used in the ready-to-use dye composition is not critical. They can be chosen, in particular, from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

Among the para-phenylenediamines which can be used as oxidation base in the dye compositions in accordance with the invention, mention may be made in particular of the compounds of formula (III) below, and the addition salts thereof with an acid:



(III)

in which:

- R_{10} represents a hydrogen atom or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical, (C_1-C_4)alkoxy(C_1-C_4)alkyl radical, C_1-C_4 alkyl radical substituted with a nitrogenous group, phenyl or 4'-aminophenyl;
- R_{11} represents a hydrogen atom or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical, (C_1-C_4)alkoxy(C_1-C_4)alkyl radical or C_1-C_4 alkyl radical substituted with a nitrogenous group;
- R_{12} represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_1-C_4 hydroxyalkoxy radical, acetylamino(C_1-C_4)alkoxy, mesylamino(C_1-C_4)alkoxy or carbamoylamino(C_1-C_4)alkoxy radical,
- R_{13} represents a hydrogen or halogen atom or a C_1-C_4 alkyl radical.

Among the nitrogenous groups of formula (III) above, mention may be made in particular of amino, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino,

tri(C_1-C_4)alkylamino, monohydroxy(C_1-C_4)alkylamino, imidazolinium and ammonium radicals.

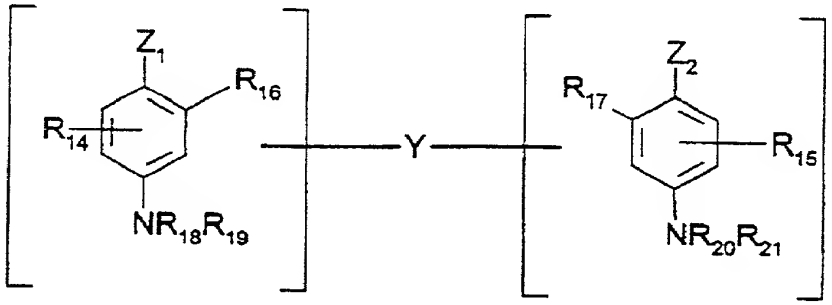
Among the para-phenylenediamines of formula (III) above, mention may be made more particularly of para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-(β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine and N-(β-methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

Among the para-phenylenediamines of formula (III) above, the ones most particularly preferred are

para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2-β-acetylaminoethyloxy-para-phenylenediamine, and the addition salts thereof with an acid.

According to the invention, the term "double bases" means compounds comprising at least two aromatic nuclei on which amino and/or hydroxyl groups are borne.

Among the double bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to the formula (IV) below, and the addition salts thereof with an acid:



(II)

in which:

- Z_1 and Z_2, which may be identical or different, represent a hydroxyl or $-NH_2$ radical which can be substituted with a C_1-C_4 alkyl radical or with a linker arm Y;

- the linker arm Y represents a linear or branched alkylene chain comprising from 1 to 14 carbon atoms, which can be interrupted or terminated with one or more nitrogenous groups and/or with one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C_1-C_6 alkoxy radicals;
- R_{14} and R_{15} represent a hydrogen or halogen atom, a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical or C_1-C_4 aminoalkyl radical or a linker arm Y;
- R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21}, which may be identical or different, represent a hydrogen atom, a linker arm Y or a C_1-C_4 alkyl radical;

it being understood that the compounds of formula (IV) comprise only one linker arm Y per molecule.

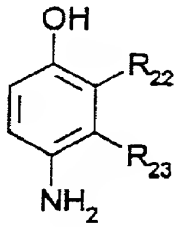
Among the nitrogenous groups of formula (IV) above, mention may be made in particular of amino, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, tri(C_1-C_4)alkylamino, monohydroxy(C_1-C_4)alkylamino, imidazolinium and ammonium radicals.

Among the double bases of formula (IV) above, mention may be made more particularly of N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)-

tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

Among these double bases of formula (IV), N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, or one of the addition salts thereof with an acid, are particularly preferred.

Among the para-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds of formula (V) below, and the addition salts thereof with an acid:



(V)

in which:

- R_{22} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, (C_1-C_4)alkoxy(C_1-C_4)alkyl, C_1-C_4 aminoalkyl or hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radical,

- R_{23} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 aminoalkyl, cyano(C_1-C_4)alkyl or (C_1-C_4)alkoxy(C_1-C_4)alkyl radical,

it being understood that at least one of the radicals R_{22} and R_{23} represents a hydrogen atom.

Among the para-aminophenols of formula (V) above, mention may be made more particularly of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

Among the ortho-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

Among the heterocylic bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in GB patents 1,026,978 and 1,153,196, such as 2-5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β-methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

Among the pyrimidine derivatives, mention may be made more particularly of the compounds described, for example, in German patent DE 2,359,399 or Japanese patents JP 88-169,571 and JP 91-333,495 or patent applications WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-traminopyrimidine, and pyrazolopyrimidine derivatives, such as those mentioned in patent application FR-A-2,750,048 and among which mention may be made of pyrazolo[1,5-a]pyrimidine-3,7-diamine; 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidin-7-ol; 3-aminopyrazolo[1,5-a]pyrimidin-5-ol; 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-

hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 2,5, N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists, and the addition salts thereof with an acid.

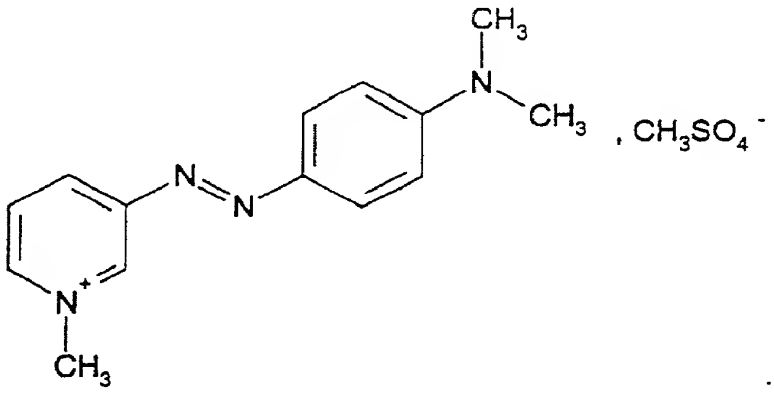
Among the pyrazole derivatives, mention may be made more particularly of the compounds described in patents DE 3,843,892 and DE 4,133,957 and patent applications WO 94/08969, WO 94/08970, FR-A-2,733,749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β-hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

The oxidation base(s) preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition in accordance with the invention, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

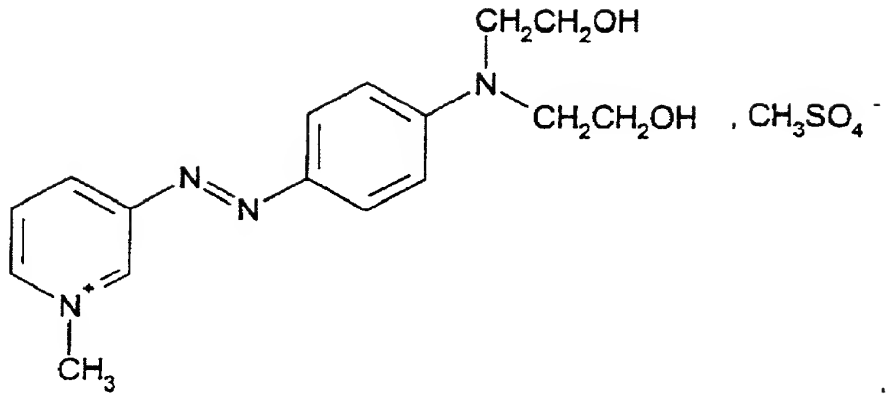
The 3-aminopyridine derivative(s) of formula (I) in accordance with the invention is (are) preferably chosen from:

- 4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



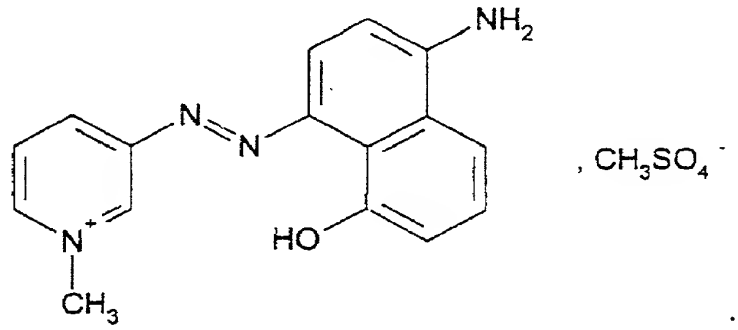
;

- 4'-bis(β-hydroxyethyl)aminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



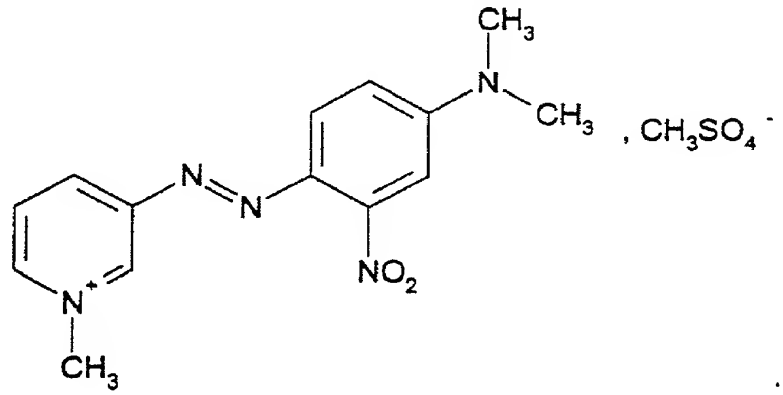
;

- 4'-amino-8'-hydroxynaphthalene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



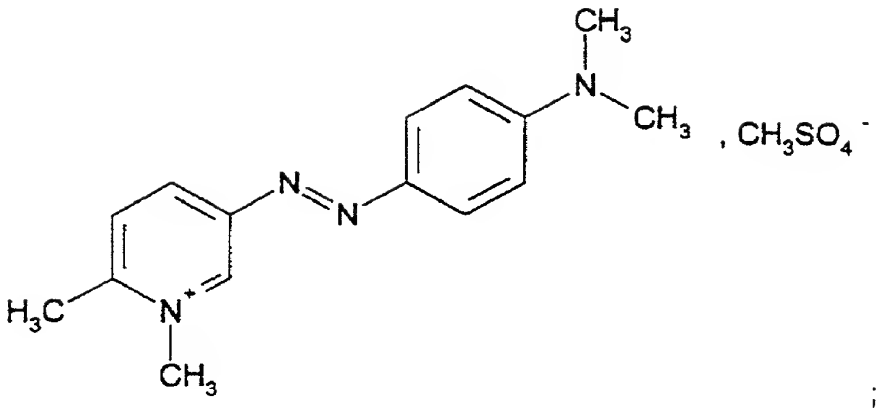
;

- 4'-dimethylamino-2'-nitrobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



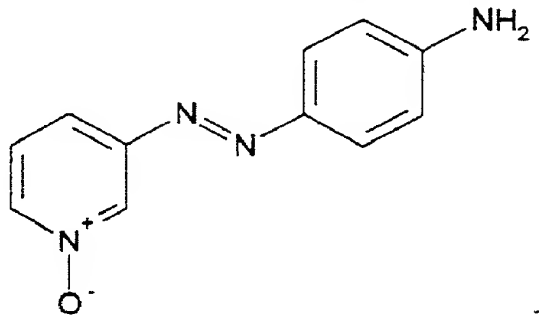
;

- 4'-dimethylaminobenzene-1'-azo-1,6-dimethyl-3-pyridinium methosulphate of formula:



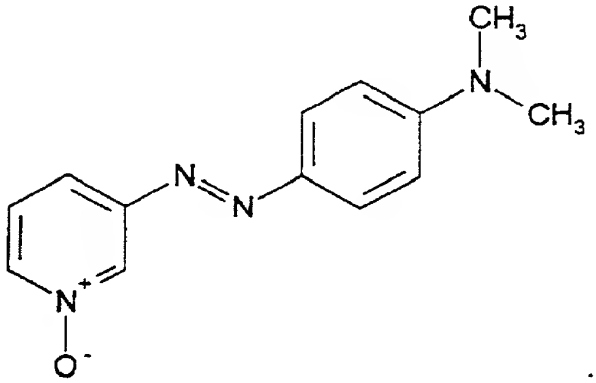
;

- 4'-aminobenzene-1'-azo-3-pyridine N-oxide of formula:



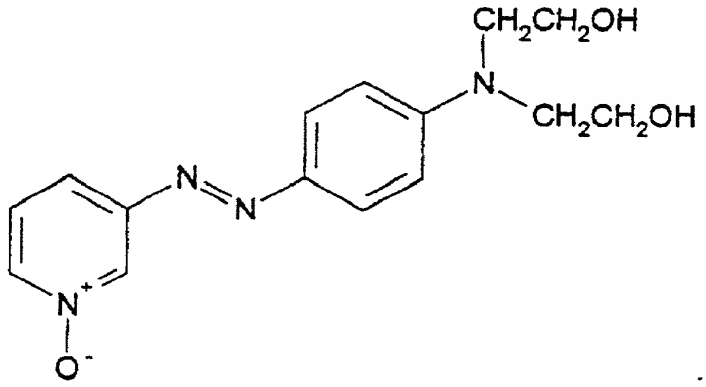
;

- 4'-dimethylaminobenzene-1'-azo-3-pyridine N-oxide of formula:



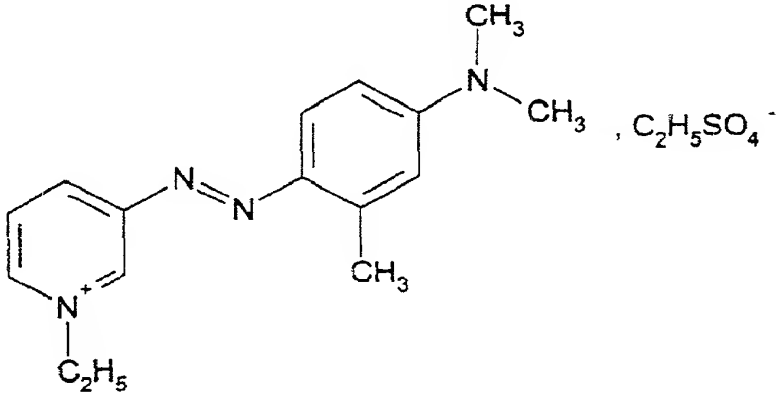
;

- 4'-N,N-bis(β-hydroxyethyl)aminobenzene-1'-azo-3-pyridine N-oxide of formula:



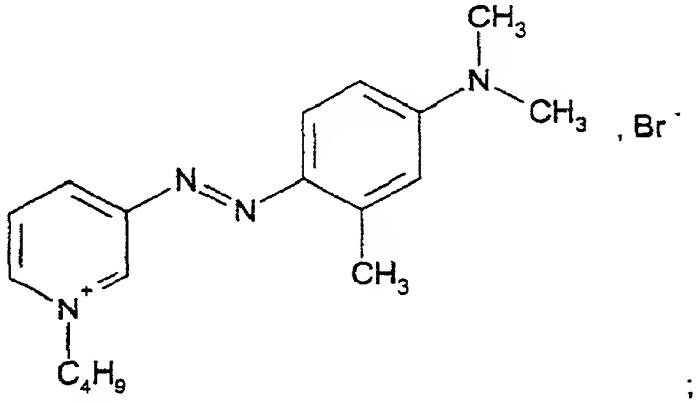
;

- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:



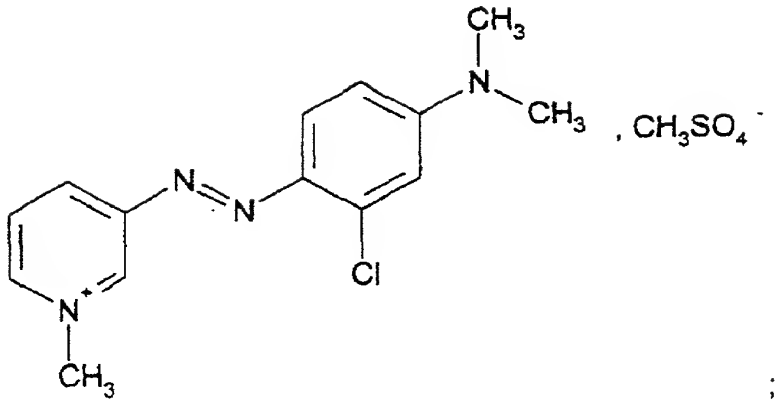
;

- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-butyl-3-pyridinium bromide of formula:



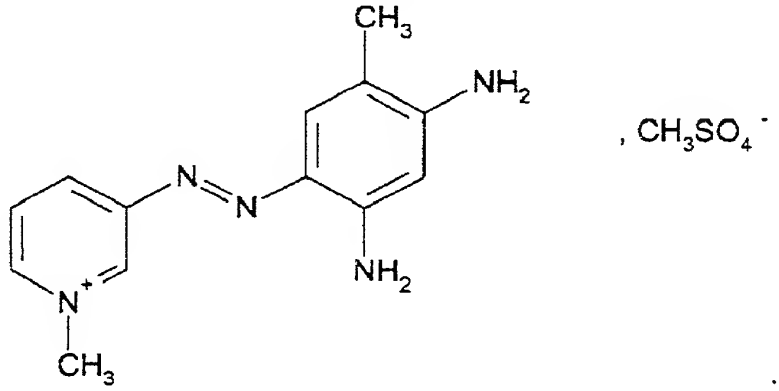
;

- 4'-dimethylamino-2'-chlorobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



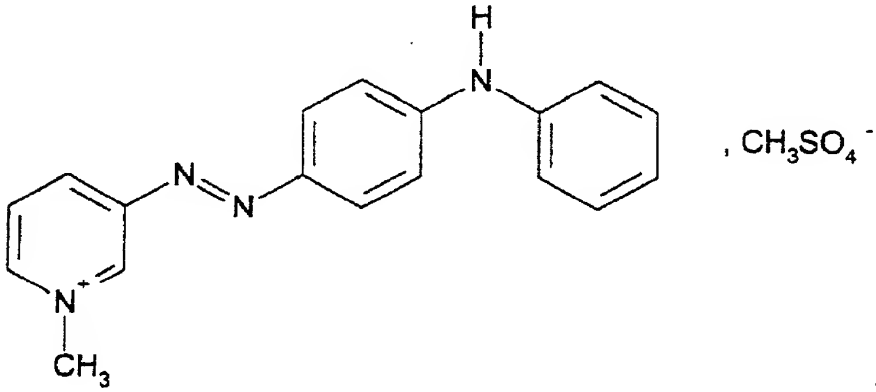
;

- 2',4'-diamino-5'-methylbenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



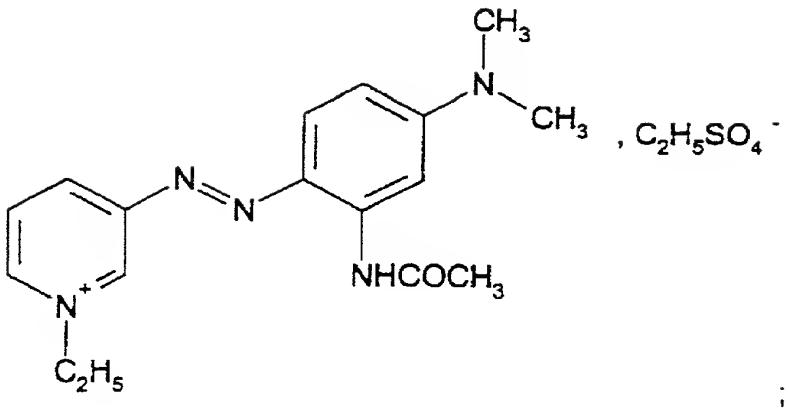
;

- 4'-phenylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

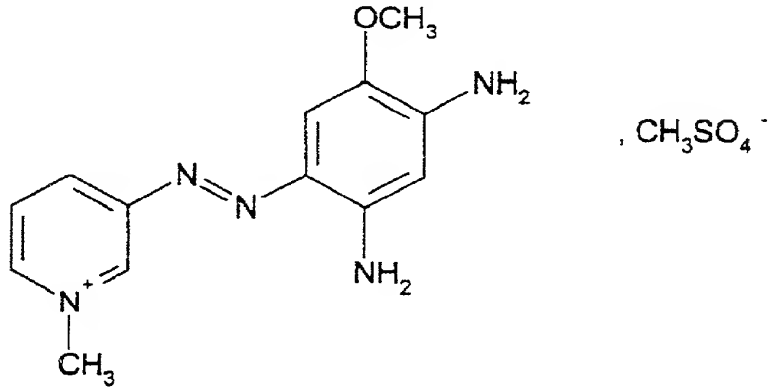


;

- 2'-acetylamino-4'-dimethylaminobenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:

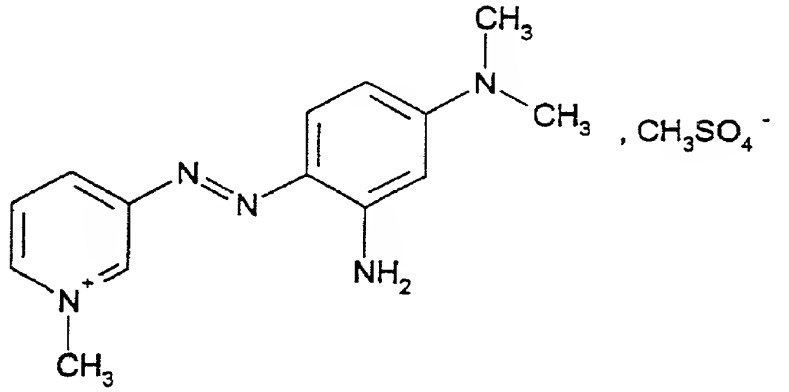


- 2',4'-diamino-5'-methoxybenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



and

- 2'-amino-4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



The 3-aminopyridine derivative(s) of formula (I) used according to the invention preferably

represent(s) from 0.001 to 10% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.01 to 5% by weight approximately relative to this weight.

Among the meta-aminophenols of formula (II) above, mention may be made more particularly of 5-amino-2-methoxyphenol, 5-amino-2-(β-hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol, 5-(γ-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-amino-6-chlorophenol and 3-(β-aminoethyl)amino-6-chlorophenol, and the addition salts thereof with an acid.

The meta-aminophenol derivative(s) of formula (II) in accordance with the invention preferably represent(s) from 0.0001 to 10% by weight approximately relative to the total weight of the dye composition and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

The dye composition in accordance with the invention can also contain one or more couplers other than the meta-aminophenol derivatives of formula (II) and/or one or more direct dyes other than the 3-aminopyridine derivatives of formula (I), in

particular to modify the shades or to enrich them with glints.

Among the couplers which may also be present in the dye composition in accordance with the invention, mention may be made in particular of meta-phenylenediamines, meta-diphenols and heterocyclic couplers, and the addition salts thereof with an acid.

When they are present, these additional couplers preferably represent from 0.0001 to 10% by weight approximately relative to the total weight of the dye composition and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The medium which is suitable for dyeing (or support) for the dye composition in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently soluble in water. Organic solvents which may be mentioned, for example, are C_1-C_4 alkanols, such as ethanol and isopropanol.

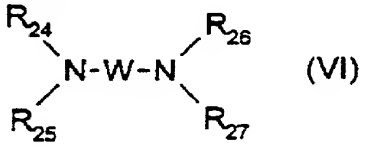
The solvents can be present in proportions preferably of between 1 and 40% by weight approximately

relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the dye composition in accordance with the invention is generally between 3 and 12 approximately, and preferably between 5 and 12 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents usually used for dyeing keratin fibres.

Among the acidifying agents which may be mentioned, for example, are inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid or lactic acid, and sulphonic acids.

Among the basifying agents which may be mentioned, for example, are aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamine, 2-methyl-2-aminopropanol and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (VI) below:



(VI)

in which W is a propylene residue optionally substituted with a hydroxyl group or a C_1-C_4 alkyl radical; R_{24}, R_{25}, R_{26} and R_{27}, which may be identical or

different, represent a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 hydroxyalkyl radical.

The dye composition in accordance with the invention can also contain various adjuvants conventionally used in compositions for dyeing the hair.

Needless to say, a person skilled in the art will take care to select this or these optional additional compounds such that the advantageous properties intrinsically associated with the dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition or additions envisaged.

The dye composition in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which are optionally pressurized, or in any other form which is suitable for dyeing keratin fibres, and in particular human hair.

A subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the dye composition as defined above.

According to this process, the dye composition as defined above is applied to the fibres, the colour being developed at acidic, neutral or alkaline pH with the aid of an oxidizing agent which is added to the dye composition only at the time of use, or which is present in an oxidizing composition that is

applied simultaneously or sequentially in a separate manner.

According to a particularly preferred embodiment of the dyeing process according to the invention, the dye composition described above is mixed, at the time of use, with an oxidizing composition containing, in a medium which is suitable for dyeing, at least one oxidizing agent present in an amount which is sufficient to develop a coloration. The mixture obtained is then applied to the keratin fibres and is left on them for 3 to 50 minutes approximately, preferably 5 to 30 minutes approximately, after which the fibres are rinsed, washed with shampoo, rinsed again and dried.

The oxidizing agent present in the oxidizing composition as defined above can be chosen from the oxidizing agents conventionally used for the oxidation dyeing of keratin fibres, and among which mention may be made of hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates, percarbonates and persulphates, peracids, enzymes such as 2-electron oxidoreductases, peroxidases and lactases. Hydrogen peroxide is particularly preferred.

The pH of the oxidizing composition containing the oxidizing agent as defined above is such that, after mixing with the dye composition, the pH of the resulting composition applied to the keratin fibres preferably ranges between 3 and 12 approximately and

even more preferably between 5 and 11. It is adjusted to the desired value by means of acidifying or basifying agents usually used for dyeing keratin fibres and are as defined above.

The oxidizing composition as defined above can also contain various adjuvants conventionally used in compositions for dyeing the hair and as defined above.

The composition which is finally applied to the keratin fibres can be in various forms, such as in the form of liquids, creams or gels or in any other form which is suitable for dyeing keratin fibres, and in particular human hair.

Another subject of the invention is a multi-compartment dyeing device or multi-compartment dyeing "kit", or any other multi-compartment packaging system, a first compartment of which contains the dye composition as defined above and a second compartment of which contains the oxidizing composition as defined above. These devices may be equipped with a means for applying the desired mixture to the hair, such as the devices described in patent FR-2,586,913 in the name of the Applicant.

The examples which follow are intended to illustrate the invention without thereby limiting its scope.

EXAMPLES

COMPARATIVE DYEING EXAMPLES 1 TO 4

The dye compositions below were prepared (contents in grams):

EXAMPLE	1	2(*)	3	4(*)
4'-Dimethylaminobenzene-1'-azo-3-pyridine N-oxide (compound of formula (I))	0.5	0.5	-	-
2'-Acetylamino-4'-dimethyl-aminobenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate (compound of formula (I))	-	-	0.6	0.6
para-Phenylenediamine (oxidation base)	0.324	0.324	0.324	0.324
5-Amino-2-methylphenol (coupler of formula (II))	0.369	-	0.369	-
meta-Aminophenol (coupler)	-	0.327	-	0.327
Common dye support	(**)	(**)	(**)	(**)
Demineralized water qs	100 g	100 g	100 g	100 g

(*): Comparative example not forming part of the invention

(**): Common dye support:

- Oleyl alcohol polyglycerolated with 2 mol of glycerol	4.0	g
- Oleyl alcohol polyglycerolated with 4 mol of glycerol, containing 78% active material (A.M.)	5.69	g A.M.
- Oleic acid	3.0	g
- Oleylamine containing 2 mol of ethylene oxide, sold under the trade name Ethomeen O12® by the company Akzo	7.0	g
- Diethylaminopropyl laurylaminosuccinamate, sodium salt, containing 55% A.M.	3.0	g A.M.
- Oleyl alcohol	5.0	g
- Oleic acid diethanolamide	12.0	g
- Propylene glycol	3.5	g
- Ethyl alcohol	7.0	g
- Dipropylene glycol	0.5	g
- Propylene glycol monomethyl ether	9.0	g
- Sodium metabisulphite as an aqueous solution containing 35% A.M.	0.455	g A.M.
- Ammonium acetate	0.8	g
- Antioxidant, sequestering agent	qs	
- Fragrance, preserving agent	qs	
- Aqueous ammonia containing 20% NH_3	10.0	g

Each of the dye compositions described above was mixed, at the time of use, with an equivalent

weight-amount of 20-volumes hydrogen peroxide (6% by weight) having a pH of about 3.

Each resulting mixture had a pH of about 10±0.2 and was applied for 30 minutes to locks of permanent-waved grey hair containing 90% white hairs.

The hair was then rinsed with water, washed with a standard shampoo, rinsed again and then dried.

The colour of the locks was evaluated before and after dyeing, in the Munsell system, using a Minolta CM 2002® spectrophotometer.

According to the Munsell notation, a colour is defined by the formula:

HV / C

in which the three parameters denote, respectively, the "Hue" or shade (H), the "Value" or intensity (V) and the "Chroma" or saturation (C), the oblique line simply being a convention and not denoting a ratio.

The increase in the coloration ΔE can be calculated by applying the Nickerson equation:

$$\Delta E = 0.4C_0dH + 6dV + 3dC$$

as described, for example, in "Journal of the Optical Society of America", vol. 34, No. 9, Sept 1944, pages 550-570.

In this equation, ΔE represents the difference in colour between two locks (in the present case the increase in the coloration), dH, dV and dC

represent the variation in absolute value of the three parameters H, V and C, C_0 representing the saturation of the lock relative to which it is desired to evaluate the difference in colour.

The greater the value of ΔE, the greater the difference in colour between the two locks, and, in the present case, the greater the increase in the coloration (or intensity of the coloration).

The results are given in the table below:

Example	Colour of the lock before dyeing	Colour of the lock after dyeing	Increase in coloration			
			dH	dV	dC	ΔE
1	3.3 Y 5.8/1.6	6.5 R 2.7/3.8	16.8	3.1	2.2	**36.0**
2 (*)	3.3 Y 5.8/1.6	1.2 YR 2.4/2.1	12.1	3.4	0.5	**29.6**
3	3.3 Y 5.8/1.6	5.1 R 2.5/3.0	18.2	3.3	1.4	**35.6**
4 (*)	3.3 Y 5.8/1.6	8.7 R 2.2/1.5	14.6	3.6	0.1	**31.2**

(*) Comparative example not forming part of the invention

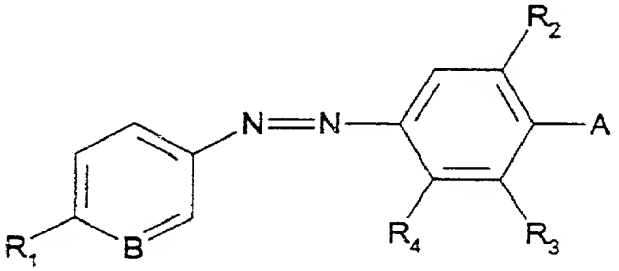
It is found that the dye compositions of Examples 1 and 3 in accordance with the invention, i.e. compositions containing a combination of a direct dye of formula (I), an oxidation base and a coupler of formula (II), lead to more intense colorations than the dye compositions of Examples 2 and 4 not forming part

of the invention since they contain an unsubstituted coupler of meta-aminophenol type and as described, for example, in patent application FR-A-2,285,851.

CLAIMS

1. Composition for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing:

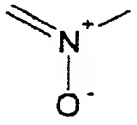
- at least one oxidation base,
- as direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I) below:



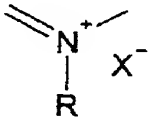
(I)

in which:

- B represents a group of formula (Ia) or (Ib) below:



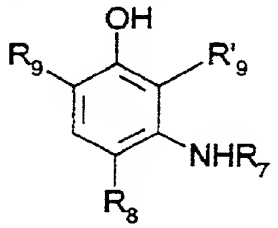
(Ia)



(Ib)

- R represents a C_1-C_4 alkyl radical;
- R_1 represents a hydrogen or halogen atom such as chlorine, bromine or fluorine, or a C_1-C_4 alkyl or C_1-C_4 alkoxy radical;
- R_2 represents a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 alkoxy radical;

- R_4 represents a hydrogen or halogen atom such as chlorine, bromine or fluorine, or a C_1-C_4 alkyl, nitro, amino or (C_1-C_4)acylamino radical;
- R_3 represents a hydrogen atom or else R_4 and R_3 together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;
- A represents a residue $-NR_5R_6$ in which R_5 represents a hydrogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical; R_6 represents a hydrogen atom, a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical, a phenyl ring or a $-CH_2-SO_3Na$ radical;
- X^- represents a monovalent or divalent anion and is preferably chosen from a halogen atom such as chlorine, bromine, fluorine or iodine, a hydroxide, a hydrogen sulphate or a (C_1-C_6)alkyl sulphate such as, for example, a methyl sulphate or an ethyl sulphate, and
- at least one coupler chosen from the meta-aminophenol derivatives of formula (II) below, and the addition salts thereof with an acid:



(II)

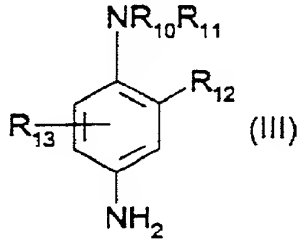
in which:

- R_7 represents a hydrogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl or C_1-C_4 monoaminoalkyl radical;
- R_8 represents a hydrogen atom, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or a halogen atom chosen from chlorine, bromine and fluorine,
- R_9 and R'_9, which may be identical or different, represent a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 monohydroxyalkoxy or C_2-C_4 polyhydroxyalkoxy radical;

it being understood that at least one of the radicals R_7, R_8, R_9 and R'_9 is other than a hydrogen atom.

2. Composition according to Claim 1, characterized in that the oxidation base(s) is (are) chosen from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

3. Composition according to Claim 2, characterized in that the para-phenylenediamines are chosen from the compounds of formula (III) below, and the addition salts thereof with an acid:



(III)

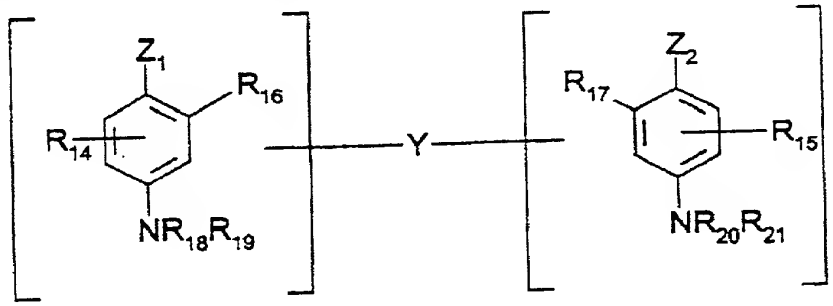
in which:

- R_{10} represents a hydrogen atom or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical, (C_1-C_4)alkoxy(C_1-C_4)alkyl radical, C_1-C_4 alkyl radical substituted with a nitrogenous group, phenyl or 4'-aminophenyl;
- R_{11} represents a hydrogen atom or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical, (C_1-C_4)alkoxy(C_1-C_4)alkyl radical or C_1-C_4 alkyl radical substituted with a nitrogenous group;
- R_{12} represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_1-C_4 hydroxyalkoxy radical, acetylamino(C_1-C_4)alkoxy, mesylamino(C_1-C_4)alkoxy or carbamoylamino(C_1-C_4)alkoxy radical,
- R_{13} represents a hydrogen or halogen atom or a C_1-C_4 alkyl radical.

4. Composition according to Claim 3, characterized in that the para-phenylenediamines of formula (III) are chosen from para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-

phenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-(β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine and N-(β-methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

5. Composition according to Claim 2, characterized in that the double bases are chosen from the compounds of formula (IV) below, and the addition salts thereof with an acid:



(II)

in which:

- Z_1 and Z_2, which may be identical or different, represent a hydroxyl or $-NH_2$ radical which can be

substituted with a C_1-C_4 alkyl radical or with a linker arm Y;

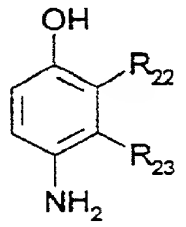
- the linker arm Y represents a linear or branched alkylene chain comprising from 1 to 14 carbon atoms, which can be interrupted or terminated with one or more nitrogenous groups and/or with one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C_1-C_6 alkoxy radicals;
- R_{14} and R_{15} represent a hydrogen or halogen atom, a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical or C_1-C_4 aminoalkyl radical or a linker arm Y;
- R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21}, which may be identical or different, represent a hydrogen atom, a linker arm Y or a C_1-C_4 alkyl radical;

it being understood that the compounds of formula (IV) comprise only one linker arm Y per molecule.

6. Composition according to Claim 5, characterized in that the double bases of formula (IV) are chosen from N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl) tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-

methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

7. Composition according to Claim 2, characterized in that para-aminophenols are chosen from the compounds of formula (V) below, and the addition salts thereof with an acid:



(V)

in which:

- R_{22} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, (C_1-C_4)alkoxy(C_1-C_4)alkyl, C_1-C_4 aminoalkyl or hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radical,
- R_{23} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 aminoalkyl, cyano(C_1-C_4)alkyl or (C_1-C_4)alkoxy(C_1-C_4)alkyl radical,

it being understood that at least one of the radicals R_{22} and R_{23} represents a hydrogen atom.

8. Composition according to Claim 7, characterized in that the para-aminophenols of formula (V) are chosen from para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol,

4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

9. Composition according to Claim 2, characterized in that the ortho-aminophenols are chosen from 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

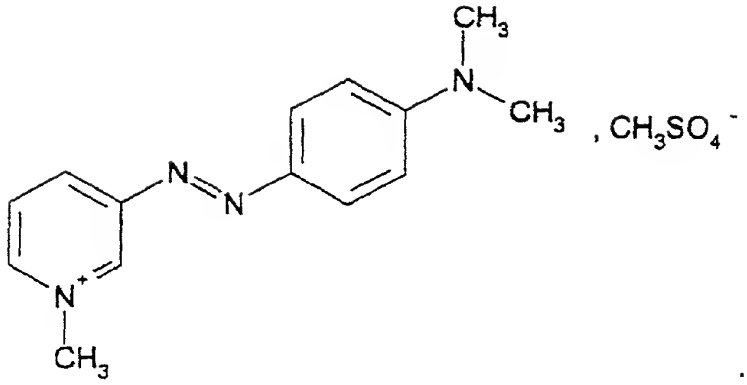
10. Composition according to Claim 2, characterized in that the heterocyclic oxidation bases are chosen from pyridine derivatives, pyrimidine derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

11. Composition according to any one of the preceding claims, characterized in that the oxidation base(s) represent(s) from 0.0005 to 12% by weight relative to the total weight of the dye composition.

12. Composition according to Claim 11, characterized in that the oxidation base(s) represent(s) from 0.005 to 6% by weight relative to the total weight of the dye composition.

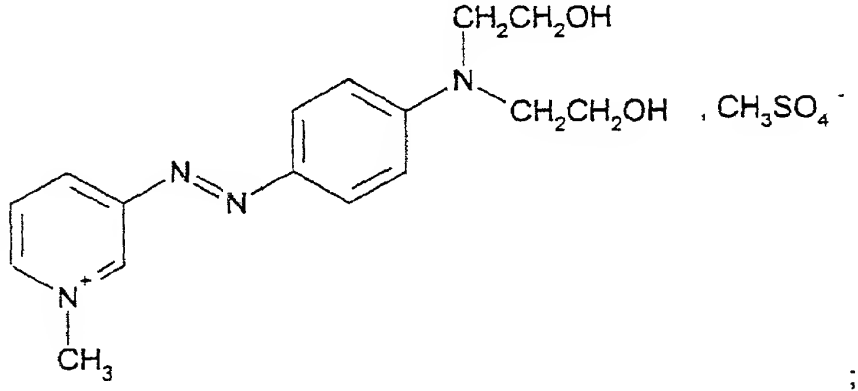
13. Composition according to any one of the preceding claims, characterized in that the 3-aminopyridine derivative(s) of formula (I) is (are) chosen from:

- 4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



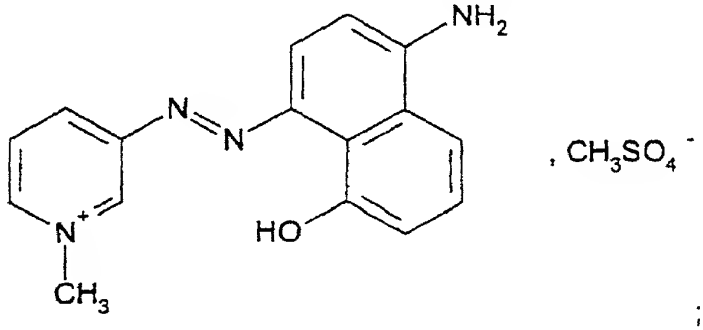
;

- 4'-bis(β-hydroxyethyl)aminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



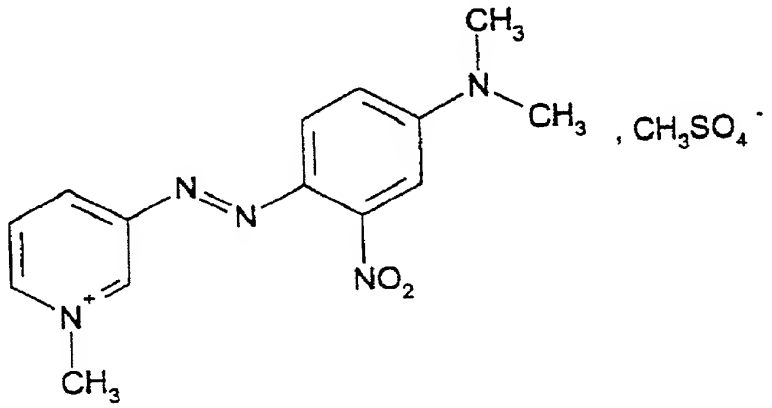
;

- 4'-amino-8'-hydroxynaphthalene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



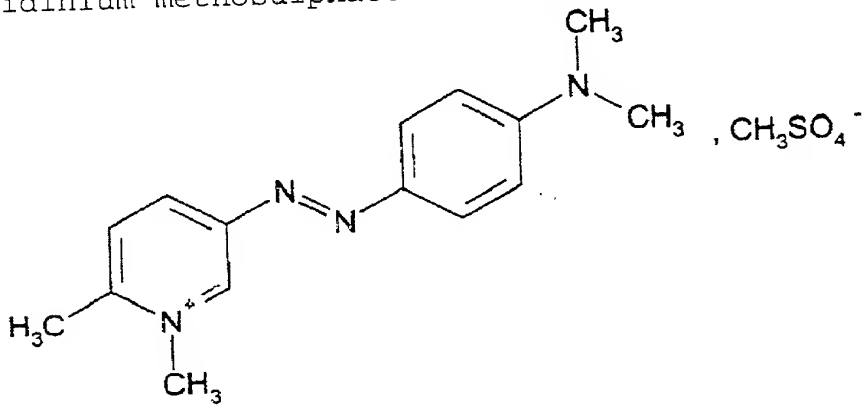
;

- 4'-dimethylamino-2'-nitrobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



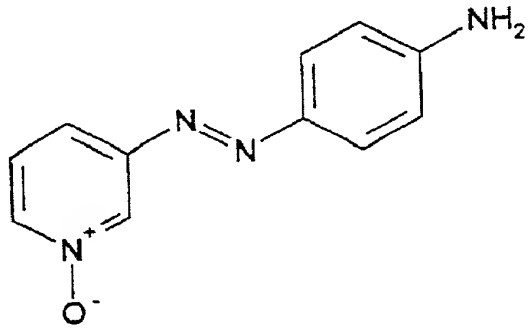
;

- 4'-dimethylaminobenzene-1'-azo-1,6-dimethyl-3-pyridinium methosulphate of formula:



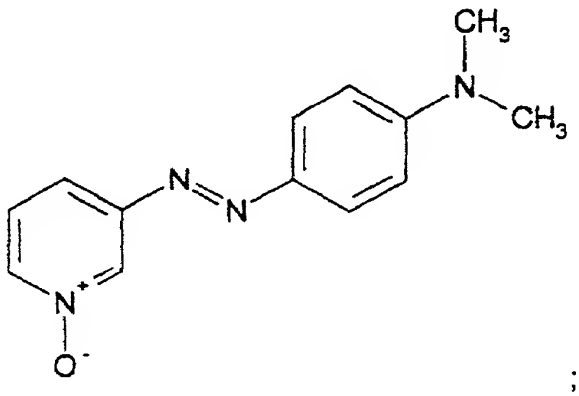
;

- 4'-aminobenzene-1'-azo-3-pyridine N-oxide of formula:



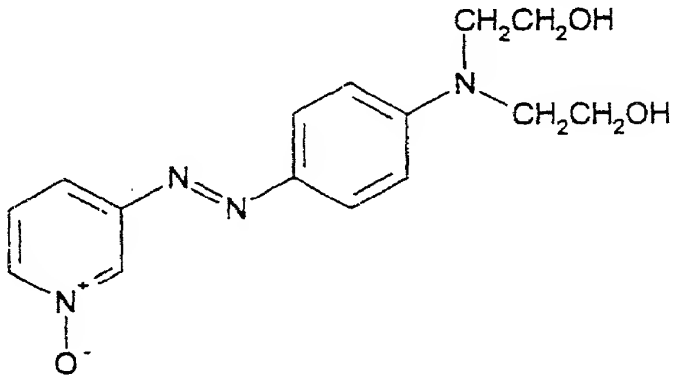
;

- 4'-dimethylaminobenzene-1'-azo-3-pyridine N-oxide of formula:



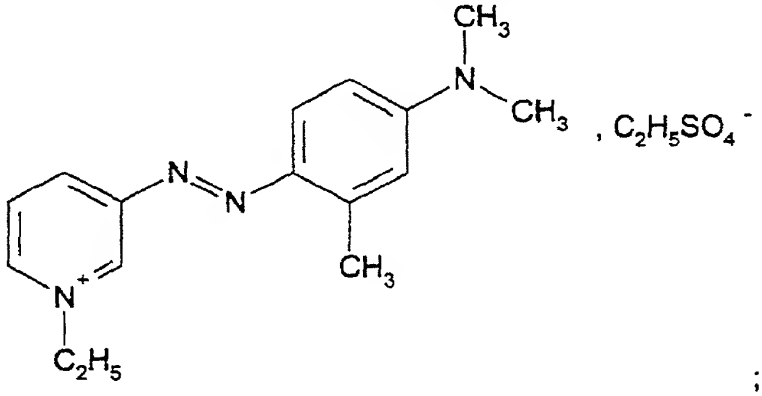
;

- 4'-N,N-bis(β-hydroxyethyl)aminobenzene-1'-azo-3-pyridine N-oxide of formula:



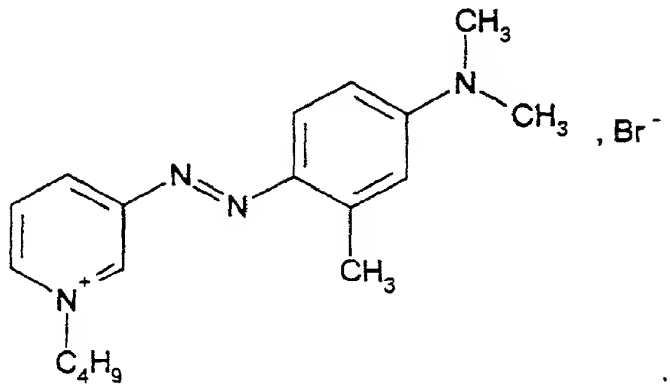
;

- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:



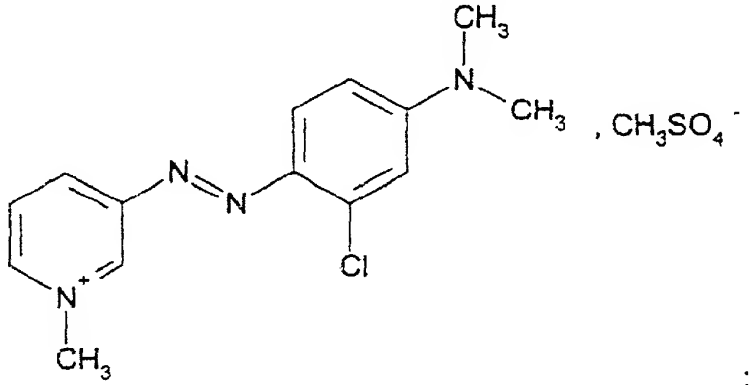
;

- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-butyl-3-pyridinium bromide of formula:



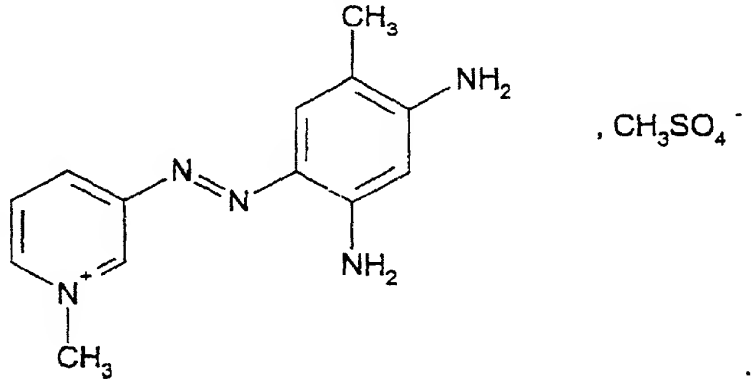
;

- 4'-dimethylamino-2'-chlorobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



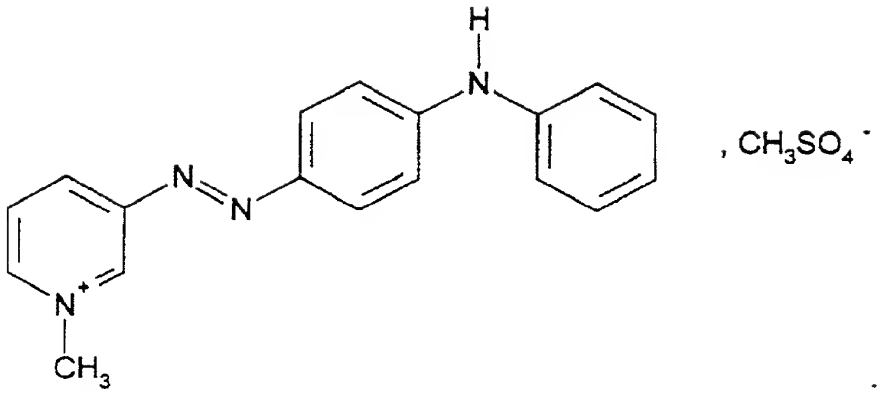
;

- 2',4'-diamino-5'-methylbenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



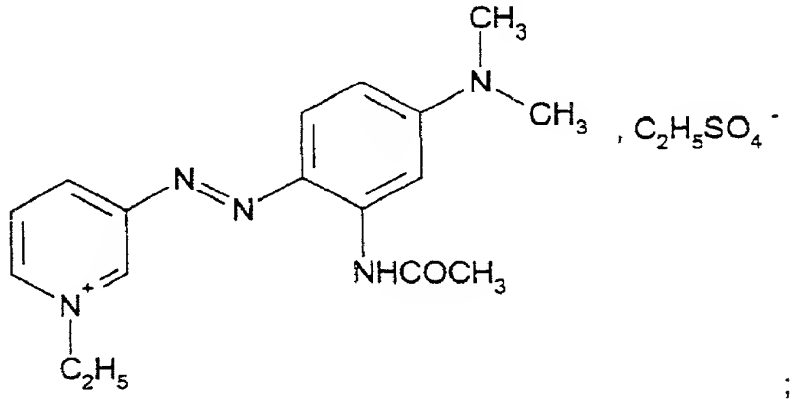
;

- 4'-phenylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



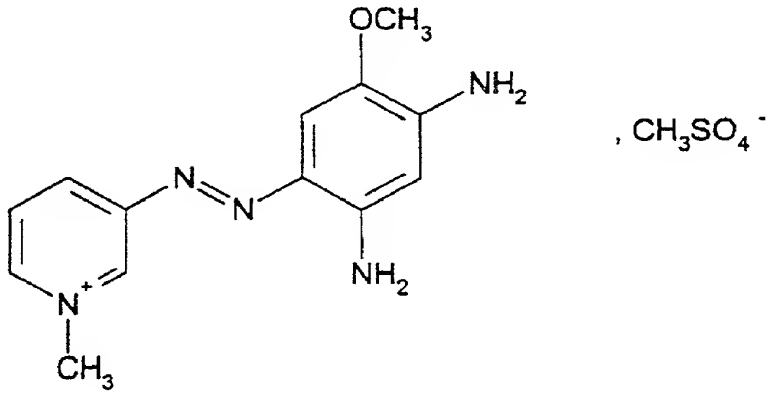
;

- 2'-acetylamino-4'-dimethylaminobenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:



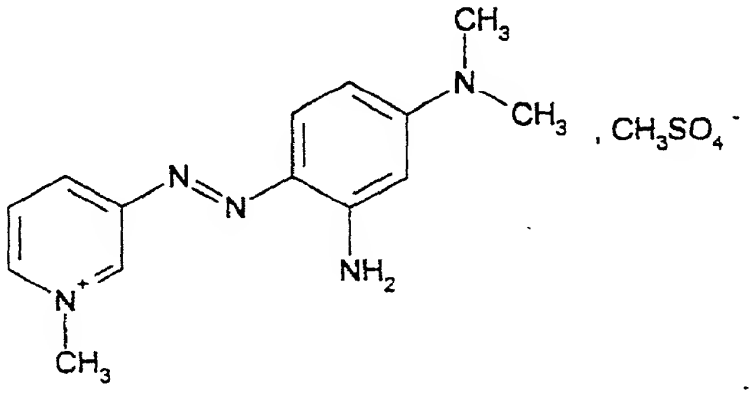
;

- 2',4'-diamino-5'-methoxybenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



and

- 2'-amino-4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



14. Composition according to any one of the preceding claims, characterized in that the 3-amino-pyridine derivative(s) of formula (I) represent(s) from 0.001 to 10% by weight relative to the total weight of the dye composition.

15. Composition according to Claim 14, characterized in that the 3-aminopyridine derivative(s) of formula (I) represent(s) from 0.01 to 5% by weight relative to the total weight of the dye composition.

16. Composition according to any one of the preceding claims, characterized in that the meta-aminophenol derivatives of formula (II) are chosen from 5-amino-2-methoxyphenol, 5-amino-2-(β-hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol, 5-(γ-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-amino-6-chlorophenol and 3-(β-

aminoethyl)amino-6-chlorophenol, and the addition salts thereof with an acid.

17. Composition according to any one of the preceding claims, characterized in that the meta-aminophenol derivative(s) of formula (II) represent(s) from 0.0001 to 10% by weight relative to the total weight of the dye composition.

18. Composition according to Claim 17, characterized in that the meta-aminophenol derivative(s) of formula (II) represent(s) from 0.005 to 5% by weight relative to the total weight of the dye composition.

19. Composition according to any one of the preceding claims, characterized in that it contains one or more couplers other than the meta-aminophenol derivatives of formula (II) as defined in Claim 1 and/or one or more direct dyes other than the 3-aminopyridine derivatives of formula (I) as defined in Claim 1.

20. Composition according to any one of the preceding claims, characterized in that the addition salts with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

21. Composition according to any one of the preceding claims, characterized in that the medium which is suitable for dyeing consists of water or of a mixture of water and at least one organic solvent.

22. Composition according to any one of the preceding claims, characterized in that it has a pH of between 3 and 12.

23. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that at least one dye composition as defined in any one of Claims 1 to 22 is applied to the said fibres, the colour being developed at acidic, neutral or alkaline pH with the aid of an oxidizing agent which is added to the dye composition only at the time of use, or which is present in an oxidizing composition that is applied simultaneously or sequentially.

24. Process according to Claim 23, characterized in that the oxidizing agent present in the oxidizing composition is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates, percarbonates and persulphates, peracids and enzymes.

25. Multi-compartment dyeing device or multi-compartment dyeing "kit", a first compartment of which contains a dye composition as defined in any one of Claims 1 to 22 and a second compartment of which contains an oxidizing composition.

ABSTRACT

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES AND DYEING PROCESS USING THIS COMPOSITION

The invention relates to a composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one oxidation base, at least one 3-aminopyridine derivative as direct dye, and at least one substituted meta-aminophenol as coupler, as well as to the dyeing process using this composition.

PTO/SB/105 (8-96)
Approved for use through 9/30/98 OMB 0651-0032
Patent and Trademark Office; U S DEPARTMENT OF COMMERCE

Attorney Docket No.: 05725.0489

Declaration and Power of Attorney for Patent Application

Déclaration et Pouvoir pour Demand de Brevet

French Language Declaration

En tant que l'inventeur nommé ci-après, je déclare par le présent acte que:

As a below named inventor, I hereby declare that:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

My residence, post office address and citizenship are as stated next to my name.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

OXIDATION DYEING COMPOSITION FOR KERATINOUS FIBRES CONTAINING A 3-AMINOPYRIDINE AZO DERIVATIVE AND DYEING METHOD USING SAID COMPOSITION

et dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée:

the specification of which is attached hereto unless the following box is checked:

☒ a été déposée le _____ sous le numéro de demande des Etats-Unis ou le numéro de demande international PCT _____ et modifiée _____ (les cas échéant).

☒ was filed on March 11, 1999 as United States Application Number or PCT International Application Number PCT/FR99/00542 and was amended on _____ (if applicable).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifées par toute modification dont il aura été fait référence ci-dessus.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International Application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior foreign application(s) Demande(s) de brevet antérieure(s)			Priority Not Claimed Droit de priorité non revendiqué
98/03453 (Number) (Numéro)	France (Country) (Pays)	20 March 1998 (Day/Month/Year Filed) (Jour/Mois/Anné de dépot)	☐
(Number) (Numéro)	(Country) (Pays)	(Day/Month/Year Filed) (Jour/Mois/Anné de dépot)	☐

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Application No.) (N° de demande)	(Filing Date) (Date de dépot)
(Application No.) (N° de demande)	(Filing Date) (Date de dépot)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont laquelle est devenue disponible entre la date de dépôt de la demande antérieure, et la date de dépôt de la demande nationale ou internationale PCT de la présente demande:

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International Application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose any or all information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Application No.) (N° de demande)	(Filing Date) (Date de dépot)	(Status) (patented, pending, abandoned) (Status) (breveté, en cours d'examen, abandonné)
(Application No.) (N° de demande)	(Filing Date) (Date de dépot)	(Status) (patented, pending, abandoned) (Status) (breveté, en cours d'examen, abandonné)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

French Language Declaration

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec L'Office des brevets et des marques: *(mentionner le nom et le numéro d'enregistrement).*

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this patent application and transact all business in the Patent and Trademark Office connected therewith: *(list name and registration number)*:

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P., Reg. No. 22,540, Douglas B. Henderson, Reg. No. 20,291; Ford F. Farabow, Jr., Reg. No. 20,630; Arthur S. Garrett, Reg. No. 20,338; Donald R. Dunner, Reg. No. 19,073; Brian G. Brunsvold, Reg. No. 22,593; Tipton D. Jennings, IV, Reg. No. 20,645; Jerry D. Voight, Reg. No. 23,020; Laurence R. Hefter, Reg. No. 20,827; Kenneth E. Payne, Reg. No. 23,098; Herbert H. Mintz, Reg. No. 26,691; C. Larry O'Rourke, Reg. No. 26,014; Albert J. Santorelli, Reg. No. 22,610; Michael C. Elmer, Reg. No. 25,857; Richard H. Smith, Reg. No. 20,609; Stephen L. Peterson, Reg. No. 26,325; John M. Romary, Reg. No. 26,331; Bruce C. Zotter, Reg. No. 27,680; Dennis P. O'Reilley, Reg. No. 27,932; Allen M. Sokal, Reg. No. 26,695; Robert D. Bajefsky, Reg. No. 25,387; Richard L. Stroup, Reg. No. 28,478; David W. Hill, Reg. No. 28,220; Thomas L. Irving, Reg. No. 28,619; Charles E. Lipsey, Reg. No. 28,165; Thomas W. Winland, Reg. No. 27,605; Basil J. Lewris, Reg. No. 28,818; Martin I. Fuchs, Reg. No. 28,508; E. Robert Yoches, Reg. No. 30,120; Barry W. Graham, Reg. No. 29,924; Susan Haberman Griffen, Reg. No. 30,907; Richard B. Racine, Reg. No. 30,415; Thomas H. Jenkins, Reg. No. 30,857; Robert E. Converse, Jr., Reg. No. 27,432; Clair X. Mullen, Jr., Reg. No. 20,348; Christopher P. Foley, Reg. No. 31,354; John C. Paul, Reg. No. 30,413; Roger D. Taylor, Reg. No. 28,992; David M. Kelly, Reg. No. 30,953; Kenneth J. Meyers, Reg. No. 25,146; Carol P. Einaudi, Reg. No. 32,220; Walter Y. Boyd, Jr., Reg. No. 31,738; Steven M. Anzalone, Reg. No. 32,095; Jean B. Fordis, Reg. No. 32,984; Barbara C. McCurdy, Reg. No. 32,120; James K. Hammond, Reg. No. 31,964; Richard V. Burgujian, Reg. No. 31,744; J. Michael Jakes, Reg. No. 32,824; Dirk D. Thomas, Reg. No. 32,600; Thomas W. Banks, Reg. No. 32,719; Christopher P. Isaac, Reg. No. 32,616; Bryan C. Diner, Reg. No. 32,409; M. Paul Barker, Reg. No. 32,013; Andrew Chanho Sonu, Reg. No. 33,457; David S. Forman, Reg. No. 33,694; Vincent P. Kovalick, Reg. No. 32,867; James W. Edmondson, Reg. No. 33,871; Michael R. McGurk, Reg. No. 32,045; Joann M. Neth, Reg. No. 36,363; Gerson S. Panitch, Reg. No. 33,751; Cheri M. Taylor, Reg. No. 33,216; Charles E. Van Horn, Reg. No. 40,266; Linda A. Wadler, Reg. No. 33,218; Jeffrey A. Berkowitz, Reg. No. 36,743; Michael R. Kelly, Reg. No. 33,921; and James B. Monroe, Reg. No. 33,971; **and** Thalia V. Warnement, Reg. No. 39,064; Michele C. Bosch, Reg. No. 40,524; Allen R. Jensen, Reg. No. 28,224; Mark D. Sweet, Reg. No. 41,469; and Anthony M. Gutowski, Reg. No. 38,742.

70

Addresser toute correspondance à:

Send all Correspondence to:

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.
1300 I Street, N.W., Washington, D.C. 20005,
Telephone No. (202) 408-4000.

Addresser tout appel téléphonique à:
(*nom et numéro de téléphone*)

Direct all Telephone Calls to:
(*name and telephone number*)

Thomas L. Irving, Reg. No. 28,619
Telephone Number (202) 408-4082

Nom complet de l'unique ou premier inventeur:	Full name of sole or first inventor 1-00 Gérard LANG
Signature de l'inventeur Date	Inventor's signature Date Gerard Lang 1999 Nov. 10
Domicile	Residence 51B, rue R. Thomas, F-95390 Saint Prix, France FRX
Nationalité:	Citizenship French
Adresse postale:	Post Office Address Same as residence
Nom complet du second co-inventeur, le cas échéant:	Full name of second joint inventor, if any: 2-00 Jean COTTERET
Signature du second inventeur Date	Second Inventor's signature Date Jean COTTERET 1999, November 10th
Domicile:	Residence 13, rue du Pré Rousselin, F-78480 Verneuil-sur-Seine, France FRX
Nationalité:	Citizenship French
Adresse postale:	Post Office Address Same as residence
Nom complet du third co-inventeur, le cas échéant:	Full name of third joint inventor, if any: 3-00 Mireille MAUBRU
Signature d'inventeur Date	Third Inventor's signature Date Mireille MAUBRU 1999, November 15th
Domicile	Residence 7, avenue d'Eprèmesnil, F-78400 Chatou, France FRX
Nationalité:	Citizenship French
Adresse postale:	Post Office Address Same as residence